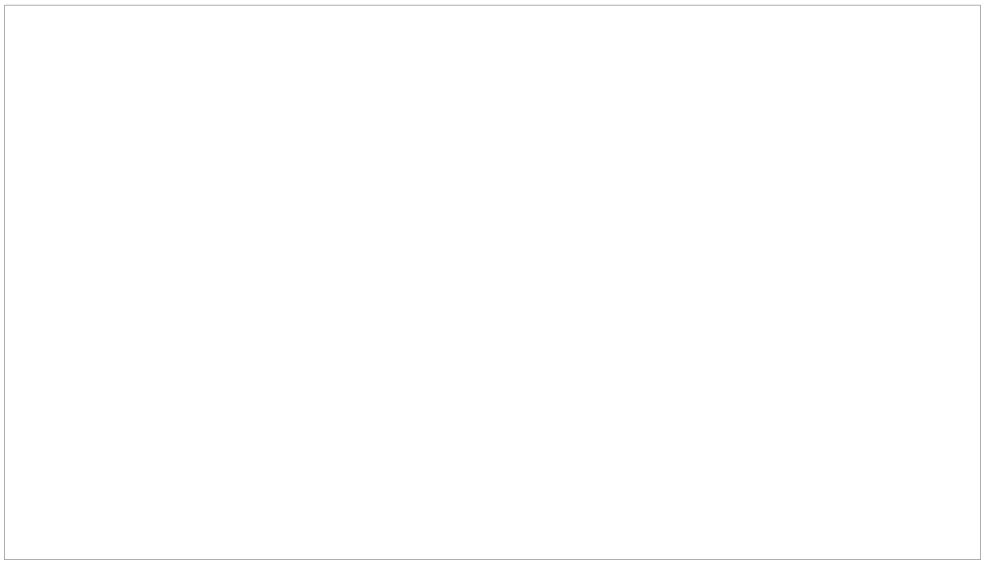

Title: ADDITION OF DIALKYLPHOSPHOROUS ACIDS TO UNSATURATED KETONES, NITRILES AND ESTERS OF ACIDS (USSR) by A. N. Punovik, and B. A. Arbuzow

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ADDITION OF DIALKYLPHOSPHOROUS ACIDS TO UNSATURATED KETONES, NITRILES, AND ESTERS OF ACIDS.

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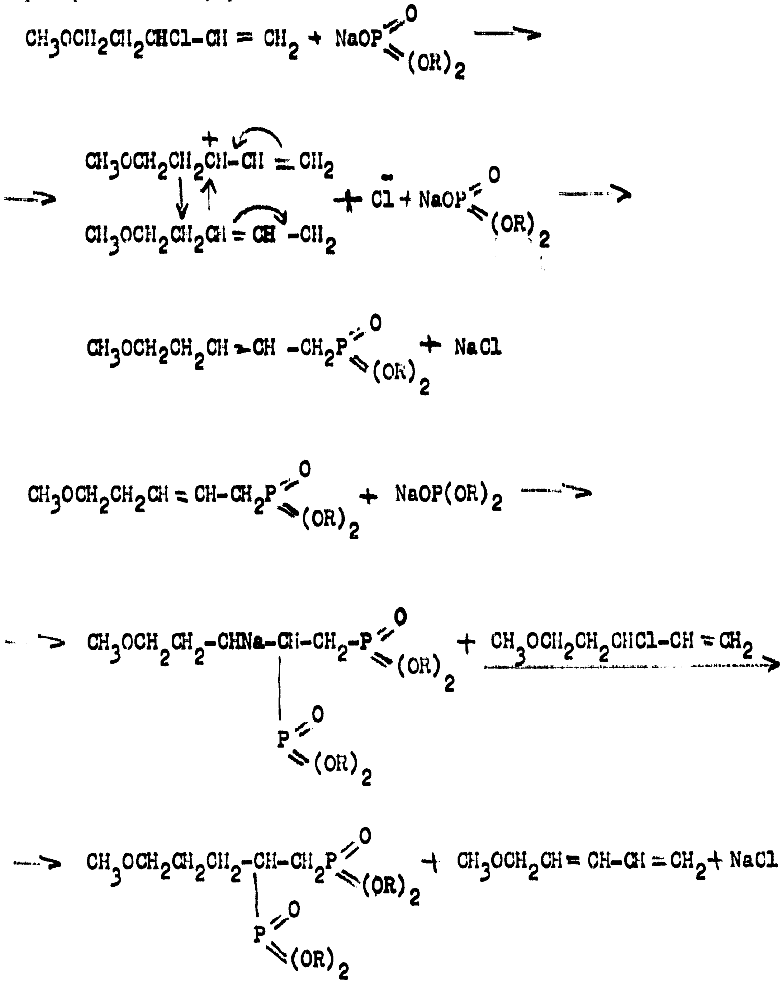
pp 327-330]

[This is another paper reporting results of the extensive investigation on organic phosphorous compounds being carried out by the team of investigators in question at Kazan'. Compounds having cholinesterase inhibitor activity (nerve poisons) and substances which may serve as intermediates in the synthesis of such compounds are being prepared and their chemical properties studied in the course of this investigation. It is not stated in any of the papers published by this group that this is actually the application which the authors have in view: this refers to a possible and potential application of the authors' results]

In one of our preceding works (1) we studied the action of dialkylphosphorous acids on isomeric methoxychloropentenes which are isomers of the allylic type. It was established that the primary chloride 1-Methoxy 5-chloropentane -3 reacts with salts of dialkylphosphorous acids according to a normal scheme, without regrouping, and with the formation of corresponding 1-methoxy- 5-dialkylphosphonic acid - 3-pentanes. The secondary

chloride 1-methoxy- 3 chloropentane - 4, in the presence of free dialkylphosphorous acids in the reaction medium reacts abnormally with salts of dialkylphosphorous acids, with complete allylic regrouping and the formation of products identical in structure with those obtained from the primary chloride. In the absence of free dialkylphosphorous acids there takes place a further addition of sodium dialkylphosphite at the double bond of 1-methoxy - 5-dialkylphosphonic acid- 3-pentenes with the formation of alkoxy (dialkylphosphonic acid) pentanes.



Because the specified case of addition of sodium salts of dialkylphosphorous acids to unsaturated compounds is up to the present time the only one reported in literature and because it offers considerable theoretical interest (since it opens a new means for the synthesis of esters of phosphonic acids containing different functional groups), we decided to study more extensively this new type of reactions in the instance of unsaturated compounds belonging to various groups of organic compounds, primarily unsaturated ketones, nitriles, and esters.

The indicated unsaturated compounds are typical electrophilic reagents possessing double bonds which are extremely active with respect to addition. Their component groups CO, CN, and COOR, in consequence of their strong electron affinity create a powerful positive charge on the beta-hydrocarbon of the ethylene bond, thereby providing favorable conditions for the addition of nucleophilic reagents to this bond. On the other hand, the ability of the functional groups in unsaturated ketones, intriles, and esters to add nucleophylic reagents is considerably reduced in comparison with similar compounds of a saturated character.

As a result of work conducted in the course of the last two years, we have shown that dialkylphosphorous acids in the presence of alcoholates of alkaline metals add readily at the double bonds of unsaturated ketones, nitriles, esters, and certain other unsaturated compounds.

In the present report are described the results of the addition of various dialkylphosphorous acids to beta, beta-dimethyl-divinylketone, the nitrile of acrylic acid, and the methyl ester of methacrylic acid.

The reactions were carried out in such a manner that a saturated alcoholic solution of sodium alcoholate was added to the mixture of equimolecular quantities of the unsaturated compound and dialkylphosphorous acid.

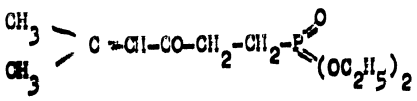
The reactions usually proceed violently with a considerable evolution of heat by the reactive mixture, and are often accompanied by boiling. The greater the molecular weight of the dialkylphosphorous acid being added, the less is the heat effect observed in the reactive process and the greater the quantity of catalyst required for bringing the reaction to completion. To separate the products of the reaction, the reaction mixture is distilled in vacuum some time after the end of the reaction.

It is necessary to note that it is advisable to employ as catalysts in the reactions under consideration sodium alcoholates of alcohols having the same radicals which enter into the composition of the dialkylphosphorous acids being added, because in this case the exchange reaction between alcohols and dialkylphosphorous acid is eliminated, thus guaranteeing the purity of the obtained product.

The addition of dimethylphosphorous, diethylphosphorous, diisobutylphosphorous, and dibutylphosphorous acids to dimethyldivinylketone was studied.

For clarification of the constitution of the products obtained, the product of addition of diethylphosphorous acid was subjected to detailed study. By titration of the product with bromine the presence of one double bond in it was established. By saponification of the product with hydrochloric acid there was obtained ethylchloride, corresponding in quantity to that computed under assumption of the presence of one diethylphosphonic group in the molecule. In the products of saponification no traces were found of phosphoric acid, which should have formed in the event that the phosphonic group in the product were attached to the carbon atom in alpha-position to the ketone group. The presence of the keto group in the product was proved by color reactions with sodium nitroprusside, beta-naphthol, and the preparation of a phenylhydrazone.

On the basis of the data obtained, the following formula was assigned to the product of the addition of diethylphosphorous acid to beta$_1$ beta-diemethyl-divinylketone:

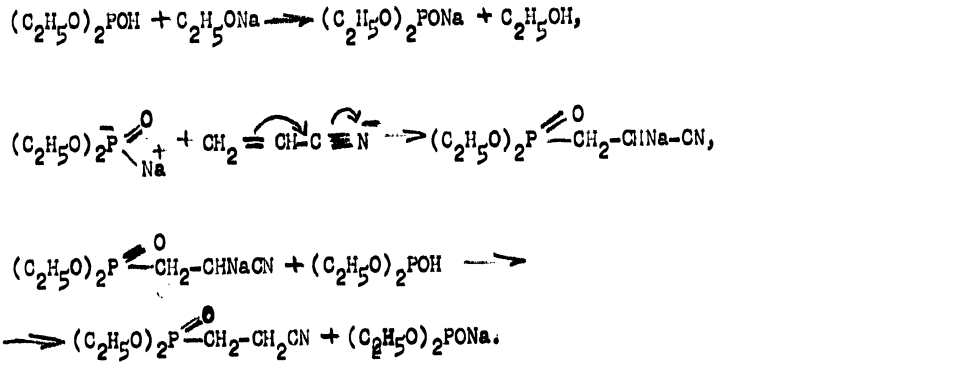


The constants and yields of all addition products obtained are presented in Table 1.

The addition of dialkylphosphorous acids to the nitrile of acrylic acid proceeds much more vigorously than the addition to beta$_1$ beta-dimethyldivinyl-ketone.

Upon the addition of several drops of a solution of an alcoholate to the reaction mixture the latter heats up strongly and moreover, in the absence of external cooling, boils violently. By saponification of the addition product obtained, phosphonopropionic acid with a melting point of 164-165° was produced.

The addition reaction can be expressed by the following scheme:



The constants and yields of the products of addition of various dialkyl-phosphorous acids to the nitrile of acrylic acid are listed in Table 2.

As we established further, dialkylphosphorous acids in the presence of alcoholates of alkaline metals are capable of being added also to esters

of unsaturated acids. In the case of the methyl ester of methacrylic acid, the addition takes place with considerably more difficulty than in the case of the nitrile of acrylic acid and beta$_1$ beta-dimethyldivinylketone; the reactions are started only by the addition of a considerable quantity of a solution of sodium alcoholate to the reaction mixture.

The constants and yields of the products obtained are given in Table 3.

The mechanism of the addition reactions can be represented by equations analogous to those given above for the case of the addition to acrylic acid nitrile.

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27 April 1950

Literature cited

A. N. Pudovik and B. A. Arbuzov, Izv. AN SSSR, OKhN, 522 (1942)

[tables attached]

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Table 1

Formula	Boiling Pt. °C/mm Hg	n_D^{20}	d_4^{20}	Yield in %
$(CH_3)_2C=CH-CO-CH_2-CH_2-P(=O)(OCH_3)_2$	169-171/13	1.4711	1.1130	59
$(CH_3)_2C=CH-CO-CH_2-CH_2-P(=O)(OC_2H_5)_2$	149/3	1.4660	1.0658	62
$(CH_3)_2C=CH-CO-CH_2-CH_2-P(=O)(OC_4H_9\text{-iso})_2$	188-189/10	1.4511	1.0013	48.5
$(CH_3)_2C=CH-CO-CH_2-CH_2-P(=O)(OC_4H_9\text{-}n)_2$	198-200/10	1.4623	0.0111	57

Table 2

$CN-CH_2-CH_2-P(=O)(OCH_3)_2$	158/11	1.4432	1.1964	86.3
$CN-CH_2-CH_2-P(=O)(OC_2H_5)_2$	159-160/10	1.4388	1.1089	83.0
$CN-CH_2-CH_2-P(=O)(OC_3H_7\text{-iso})_2$	160/13	1.4345	1.0500	46.4
$CN-CH_2-CH_2-P(=O)(OC_4H_9\text{-iso})_2$	171/11	1.4386	1.0959	71.0
$CN-CH_2-CH_2-P(=O)(OC_4H_9\text{-}n)_2$	177-178/11	1.4395	1.0455	71.5

Table 3

$CH_3OOC-CH(CH_3)-CH_2-P(=O)(OCH_3)_2$	137-138/10	1.4377	1.1761	77.7
$CH_3OOC-CH(CH_3)-CH_2-P(=O)(OC_2H_5)_2$	152-153/15	1.4350	1.1212	74.5
$CH_3OOC-CH(CH_3)-CH_2-P(=O)(OC_3H_7\text{-iso})_2$	153-154/16	1.4298	1.0612	61.0